Abstract No. chri0218

Phase Changes of Basic Bismuth(III) Nitrates Investigated by *In-Situ* X-ray Powder Diffraction

Axel Nørlund Christensen, Torben René Jensen, Jens-Erik Jørgensen (Dept. of Chem., Univ. of Aarhus, Denmark) and J. C. Hanson (Chem. Dept., BNL).

Beamline(s): X7B

Introduction: A number of basic bismuth(III) nitrates can be obtained in hydrolysis of bismuth(III) nitrate pentahydrate with water. The composition of the reaction products depends on the experimental conditions used in the hydrolysis reactions [1]. Three well defined reaction products are known, $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}4H_2O$, $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$, and $[Bi_6O_5(OH)_3](OH)_3(NO_3)_5{\cdot}3H_2O$. A fourth compound, with unknown crystal structure called phase X, can be made and that compound possibly contains the ion $[Bi_6O_4(OH)_4]^{6+}$. The aim of this work was to establish relations between the structures and composition of the three known compounds and phase X.

Methods and Materials: The syntheses of the compounds were studied by *in-situ* synchrotron X-ray powder diffraction at hydrothermal conditions using the MAR-diffractometer at the X7B beam line at NSLS. The reaction mixtures of bismuth(III) nitrate pentahydrate and water were housed in 0.7 mm diameter quartz glass capillaries heated with hot air and using a temperature ramp from 25 to 200°C. An internal pressure of up to 1700 kPa from a nitrogen gas cylinder insured no formation of vapour bubbles in the hydrothermal liquid. The wave length used was λ = 0.90371 Å. The powder patterns obtained were displayed as stacks of patterns showing powder lines to turn up or disappear during the experiments.

Results: Fig. 1 shows three crystalline phases in the temperature interval 25 to 115°C. The hydrolysis product formed in mixing bismuth(III) nitrate pentahydrate with water is $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}4H_2O$, and the sample contains this compound at hydrothermal conditions up to 70°C, where $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$ is formed. This latter compound is stable up to 90°C where phase X is formed, and this compound is then stable at hydrothermal conditions up to 200°C. Chemical analyses suggest that phase X has the composition $[Bi_6O_4(OH)_4](NO_3)_6$.

Acknowledgments: The work at BNL was supported by contract DE-AC02-98CH10086 with the US DOE Div. of Chemical Sciences and the Danish National Research Council (Dansync).

References: [1] A. N. Christensen, M.-A. Chevallier, J. Skibsted and B. B. Iversen, *J. Chem. Soc*., *Dalton Trans*., 265 (2000).

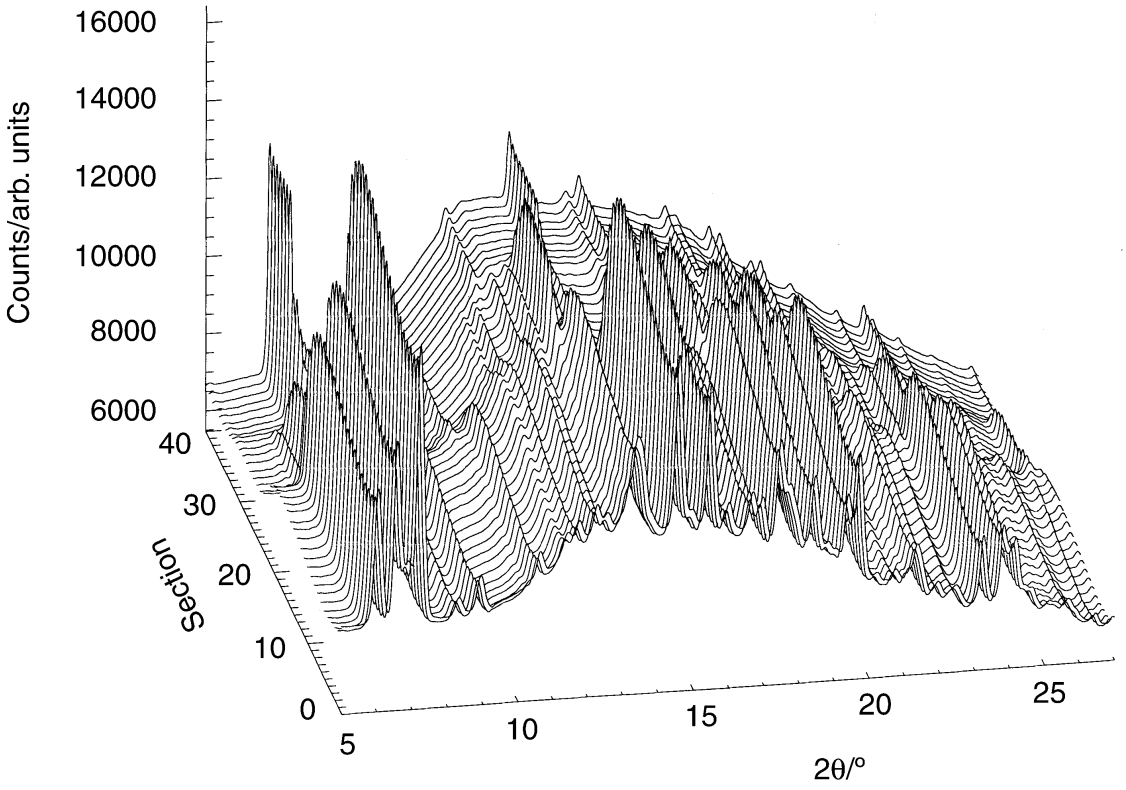

Figure 1 Three crystalline bismith(III) phases formed in the temperature interval 25 to 115°C.